# Methylenation of Carbonyl Compounds Using Chloromethyl-lithium; a New Method for Terminal and Exocyclic Olefins

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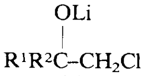
The *in situ* generated chloromethyl-lithium reacts at −78 °C with different aldehydes and ketones to afford, after lithiation with lithium powder, terminal and exocyclic olefins.

The use of methylenetriphenylphosphorane in the Wittig reaction[1] remains the most generally useful method for the conversion of carbonyl compounds into terminal olefins. Since this discovery[2] many alternative procedures have been introduced to expand the utility of this reaction.[3] We report here a new method for the direct methylenation of aldehydes and ketones using chloromethyl-lithium.[4]

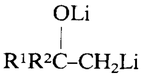
$$\underset{(1)}{R^1R^2C{=}O} \xrightarrow{\text{i, ii}} \underset{(2)}{R^1R^2C{=}CH_2}$$

**Scheme 1.** *Reagents and conditions:* i, $ClCH_2I$–MeLi, −78 to −60 °C; ii, Li, −60 to 20 °C.



$$R^1R^2\overset{\displaystyle OLi}{\overset{|}{C}}{-}CH_2Cl$$

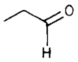
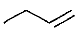
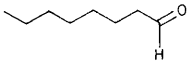
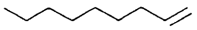
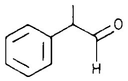
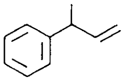
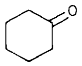
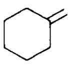
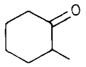
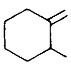
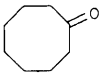
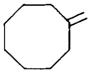
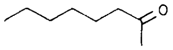
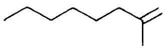
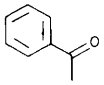
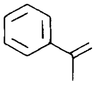
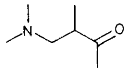
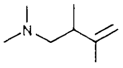
(3)



$$R^1R^2\overset{\displaystyle OLi}{\overset{|}{C}}{-}CH_2Li$$

(4)

**Table 1.** Olefins (2) from carbonyl compounds (1).

| (1) | (2) | | % Yield[a] |
|---|---|---|---|
|  |  | (2a)[b] | 43[b] |
|  |  | (2b) | 80 |
|  |  | (2c) | 55 |
|  |  | (2d) | 80 |
|  |  | (2e) | 80 |
|  |  | (2f) | 80 |
|  |  | (2g) | 95 |
|  |  | (2h) | 60 |
|  |  | (2i) | 50 |

[a] Isolated yield based on the starting carbonyl compound (1). [b] Isolated as its 1,2-dibromo derivative.

The reaction of different aldehydes and ketones (1) with chloromethyl-lithium (generated *in situ* by reaction of chloroiodomethane with methyl-lithium) at −78 °C followed by lithiation with lithium powder led to the corresponding terminal or exocyclic olefins (2)† (Scheme 1 and Table 1).

The first step in the reaction is the addition of the carbenoid to the carbonyl group[4] leading to the intermediate (3), which after lithiation gives the β-substituted organolithium compound (4);[5] the final decomposition of this system through a β-elimination process[6] yields the olefin (2). *Typical procedure:* to a solution of chloroiodomethane (11 mmol) and the starting carbonyl compound (1) (10 mmol) in tetrahydrofuran (25 ml) was added a 1 M diethyl ether solution of methyl-lithium (11 mmol) over 15 min at −78 °C under argon. The mixture was stirred for 45 min allowing the temperature to rise to −60 °C. Then lithium powder (45 mmol) was added; the resulting suspension was stirred for 6 h at the same temperature and then overnight allowing it to warm to room temperature. The mixture was hydrolysed with aqueous HCl, extracted with diethyl ether, the ethereal layer dried ($Na_2SO_4$), and the resulting residue distilled to afford the olefin (2). In the case of the product (2a) it was isolated as its 1,2-dibromo derivative following the literature method.[7]

We think that the method described in this communication represents a reasonable alternative to the Wittig reaction.

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## References

1 See, for instance, D. J. H. Smith, in 'Comprehensive Organic Chemistry,' Vol. 2, ed. I. O. Sutherland, Pergamon, Oxford, 1979, pp. 1316—1325.
2 G. Wittig and G. Geissler, *Liebigs Ann. Chem.*, 1953, **580**, 44.
3 See, for instance, R. Greenwald, U. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128; E. J. Corey and J. Kang, *J. Am. Chem. Soc.*, 1982, **104**, 4724; L. Clawson, S. L. Buchwald, and R. H. Grubbs, *Tetrahedron Lett.*, 1984, **25**, 5733.
4 R. Tarhouni, B. Kirschleger, M. Rambaud, and J. Villieras, *Tetrahedron Lett.*, 1984, **25**, 835; K. M. Sadhu and D. S. Matteson, *ibid.*, 1986, **27**, 795.
5 For stabilized intermediates of this type see, for instance, J. Barluenga, J. Flórez, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1982, 1153.
6 See, for instance, J. Barluenga, M. Yus, and P. Bernad, *J. Chem. Soc., Chem. Commun.*, 1978, 847.
7 J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Org. Chem.*, 1981, **46**, 2721.

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† All compounds (2) gave satisfactory spectral data (i.r., $^1H$ and $^{13}C$ n.m.r., and mass spectra).